Assessment of metals and anions in tap, river, wastewater, and sludge: comparison of hotplate- and microwave-assisted digestion

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In this study, the analysis of metals in tap, river, wastewater, and sludge samples was conducted using ICP–OES after hotplate- or microwave-assisted digestion. Both digestion methods produced a good degree of accuracy, indicating their suitability for the analysis of the studied metals in water samples. From method development studies, 100 mL of HNO_3 was found to be the optimum sample volume and acid type for digestion. The average concentrations obtained ranged from 4.9–410.8 µg/L, 5.9–465.0 µg/L, 3.6–425.4 µg/L, 16.1–647 µg/L and 9.7–784 µg/L in tap water, river, influent, effluent, and sludge samples, respectively. All metals were below their maximum permissible limits, with the exception of Mn in all sludge samples and Pb in all tap water, Umhlathuzana River, and Northern Works influent samples. Comparable recoveries and metal concentrations were obtained by microwave and hotplate methods, suggesting that the cheaper hotplate method can be used as an effective digestion method for daily analysis. Common anion concentrations obtained ranged from 0.03–23.5 mg/L, 0.02–3 064.67 mg/L, and 0.32–175.67 mg/L for tap, river, and wastewater samples, respectively. The anion concentrations were found to be below the maximum acceptable limits indicating no negative health effect on human and aquatic life, with the exception of Cl^- and SO_4^{2-} in Amanzimtoti and Northern River water, respectively.

INTRODUCTION

The contamination of water bodies by heavy metals can originate naturally from the weathering of minerals and rocks, or from anthropogenic sources, such as sewage discharge, urban and agricultural runoff (Jaishankar et al., 2014). Surface treatment processes using heavy metals, as well as industrial products that are discharged at the end of their life, are the major industrial sources of heavy metals that end up in wastewater. Major urban inputs to sewage water are effluents from households and businesses, and traffic-related emissions as these can be transported with stormwater into the sewerage system. These can all lead to an increased amount of heavy metals reaching wastewater treatment plants, whereafter they are discharged with the treated effluent where they may accumulate in aquatic life and enter the food chain. Also, metal contamination from river water and metal leaching from water distribution systems may lead to the presence of heavy metals in drinking water, which may result in severe human health effects, especially under significant exposure to high concentration levels (Atlas et al., 2017; Smirnova et al., 2021). Moreover, the pollution of the environment by these heavy metals is a long-term and irreversible process (Olujimi et al., 2012).

Anion (chlorides, sulphates, phosphates, nitrates, ammonia) contamination is another common environmental problem if present in high concentrations. For example, nitrates (commonly used in agricultural activities) can affect the transportation of oxygen in the blood whilst excessive phosphates can result in eutrophication and algal blooms. Chlorides are common since chlorination is a widely used water treatment process that may increase the chloride ions present in water bodies (Altundag et al., 2019). Despite chloride being an essential nutrient, high levels of consumption can lead to kidney disorders and increased blood pressure. In addition, chloride may lead to the formation of toxic disinfection by-products resulting in cancers of vital organs (Lehtonen et al., 2019).

In wastewater treatment processes, large amounts of sludge are generated and heavy metals in the wastewater influent may become concentrated in the sludge. When this sludge is used as manure on agricultural land or wastewater effluent is used for irrigation, it may transfer metals to crops. This can negatively affect the productivity of crops, and threaten animal and human health (Yamgata et al., 2010).

Despite many European countries having managed to decrease environmental pollution through the implementation of legislation, improved treatment processes, and eco-friendly industrial activities, developing countries still struggle to control environmental pollution. Therefore, new and efficient methods of treatment and consistent monitoring of water resources including wastewater are required (Olujimi et al., 2012).

Environmental sample matrices can be complex, thus requiring sample preparation prior to instrumental analysis. As a result standard acid digestion method is often used as a sample preparation method. The method is then validated by evaluating the effectiveness of metal recovery to assess the method's ability to completely digest the sample matrix (Jaishankar et al., 2014). Microwave-assisted digestion and ultrasonic digestion have become increasingly adopted due to their higher

metal recovery rate as a result of minimal sample contamination (Hu et al., 2014). Microwave-assisted digestion has several advantages over conventional hotplate digestion, including retaining volatile analytes, and rapid heating and cooling (Hu et al., 2014). Generally, an acid digestion reaction depends on several factors including the type of acid used and its concentration, the time of digestion, and the metal form present in the sample matrix (Das and Ting, 2017).

The aim of this study was therefore to compare microwave and hotplate digestion methods in terms of total dissolved and recoverable metal concentrations in different water matrices when assessing the heavy metal and anion contamination in tap, river, and wastewater. To the best of our knowledge, no reported work has been conducted to assess the concentration levels of the studied metals and anions in the selected study areas.

EXPERIMENTAL

Sample storage and collection

Tap water samples were obtained from Richmond Crest, Mkhondeni, Woodlands, Boughton and Scottsville, suburbs in the Pietermaritzburg area. River water samples were collected along the Msunduzi River, at Bishopstowe, College Road, Camp's Drift, Woodhouse, and YMCA (Fig. 1) Wastewater samples were obtained from three wastewater treatment plants (WWTPs) in the city of Durban: Amanzimtoti, Umhlathuzana and Northern. In all WWTPs, water samples were taken in the influent, the effluent and liquid sludge. The Umhlathuzana WWTP receives influent from Marianridge and Shallcross which are then combined into one effluent after treatment, and discharged into the Umhlathuzana River. Amanzimtoti WWTP discharges into the Mbokodweni River; Northern WWTP discharges into the Mgeni River. River water samples were taken from the rivers where the WWTPs of interest discharge their effluent. About 2.5 L of water was collected in polyethylene bottles and immediately placed in a portable ice chest. Samples were transported to the laboratory and filtered using a 0.45 μm membrane filter consisting of

biologically inert mixtures of cellulose acetate and cellulose nitrate (Merck, Darmstadt, Germany).

Reagents, reference materials, and standards

Ultrapure water was employed in the preparation of standard solutions for the calibration of the ICP−OES. 55% v/v nitric acid (HNO_3) (Merck, Darmstadt, Germany) was used for cleaning glassware and to digest the water samples since it liberates the trace metal elements as the soluble nitrate salt. Standard solutions were prepared by appropriate dilutions of a stock standard of 1 000 mg/L (Sigma Aldrich, South Africa). The standard reference material for trace elements in water (Ultraspec Multi-Element Aqueous CRM) was employed to evaluate the accuracy of the method employed for quantification of heavy metals in water samples.

Instrumentation

The sample digestion was performed using Multiwave 5000 (Anton Paar, Johannesburg). The Varian 720-ES ICP−OES (inductively coupled plasma−optical emission spectroscopy) was used for the determination of metals in water samples. The instrument operated at a frequency of 40 MHz and RF power of 1.00 kW, and consisted of a pneumatic concentric nebulizer with a flow rate of 0.75 L/min and a pump rate of 15 r/min. The inert carrier gas used was argon (Ar), with a plasma flow of 1.50 L/min. Three replicates were read, with a replicate read time of 1 s. These conditions remained constant throughout the analysis. Table 1 summarizes the conditions and optimal wavelengths used for each metal element.

Sample preparation

The digestion of the samples was done using a hotplate or microwave in order to determine the total recoverable and total dissolved metals in all the water samples. Spiked recovery tests were conducted for the optimization studies where the recoveries were calculated for all digestion methods.
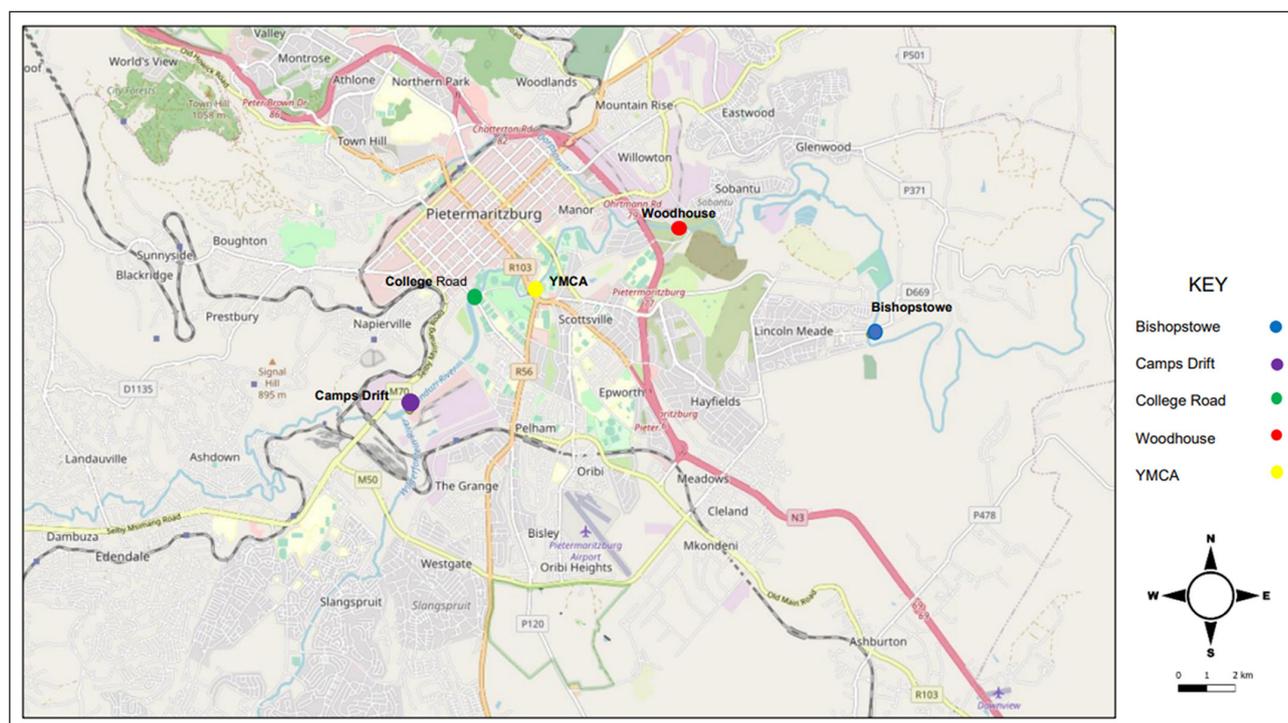
Figure 1. Map showing river water sampling points along the Msunduzi River

Table 1. Operation conditions of the ICP−OES

Specification	Operating conditions	Metal analyte	Wavelength (nm)
Manufacturer and Model	VARIAN 720-ES ICP−OES	Barium (Ba)	455.403
Frequency	40 MHz	Cadmium (Cd)	226.502
RF power	1.00 kW	Cobalt (Co)	228.615
Type of nebulizer	Pneumatic concentric nebulizer	Chromium (Cr)	267.716
Inert carrier gas	Argon	Copper (Cu)	324.754
Plasma flow rate	1.50 L/min	Gallium (Ga)	287.423
Nebulizer flow rate	0.75 L/min	Lithium (Li)	670.783
Pump rate	15 r/min	Manganese (Mn)	257.610
Replicates	3	Nickel (Ni)	231.604
Replicate read time	1 s	Lead (Pb)	220.353
		Strontium (Sr)	407.771
		Thallium (Tl)	190.807
		Zinc (Zn)	213.857

Acid digestion by heating

The United States Environmental Protection Agency (EPA 3005A) digestion method was used to determine heavy metals in water. For total recoverable metals, a 100 mL water sample was transferred into a glass beaker. 5 mL of 55% v/v nitric acid was added and the beaker heated on a hotplate to allow the contents to evaporate and reduce to around 20 mL. The sample was cooled for 5 min, and another portion of 5 mL nitric acid was added and further heated for 15 min. The sample was then cooled and transferred into a 100 mL volumetric flask and filled up to the mark with ultrapure water. For the determination of total dissolved metals, a 50 mL water sample was transferred into a 100 mL volumetric flask followed by the addition of 10 mL of 55% v/v nitric acid, and made up to the mark with ultrapure water. No heating was required for the determination of total dissolved metals as evaporation alters the amount of the sample. The samples were then analysed using ICP−OES.

Microwave-assisted acid digestion

The American Society for Testing and Materials method (ASTM-D4309-18) was followed for sample digestion to determine the total recoverable metals in water. To a 50 mL water sample, 5 mL of nitric acid was added and gently swirled. The sample−acid mixture was then digested by heating it to $170 \pm 5°C$ for 10 min and maintaining this temperature for 10 min. For the determination of total dissolved metals, the EPA 3015A method was followed. The procedure was similar to that used for the total recoverable metals; however, the microwave programme involved heating to $170 \pm 5°C$ for 20 min and maintaining this temperature for 10 min. After the digestion process was complete, the vessels were removed from the microwave reaction and transferred into ICP tubes (in a fume hood) for analysis. Both digestion methods were validated based on spiked recovery tests to assess the accuracy of the digestion methods.

Determination of anions

The Aquakem 250 discrete selective photometric analyser was employed for the determination of anions in river and wastewater samples. Sulphate (SO_4^{2-}) ions were precipitated by barium chloride in a strongly acidic medium. The resulting turbidity was measured photometrically at 405 nm. Chlorides (Cl^-) reacted with mercury (II) thiocyanate to form a soluble non-ionic compound. The thiocyanate ions released reacted with iron (III) nitrate to form a red/brown iron (III) thiocyanate complex. The resulting intensity of the stable colour produced was measured spectrophotometrically at a wavelength of 480 nm (Aquakem Labmedics, 2006; ALS, 2016). Nitrates (NO_3^-) were reduced to nitrites with hydrazine sulphate under alkaline conditions. The total nitrite ions were then reacted with sulphanilamide and N-1-naphthylenediamine hydrochloride under acidic conditions to form a pink azo-dye and the absorbance was measured at 540 nm. For the determination of phosphate ions (PO_4^{3-}), orthophosphate ions reacted with ammonium molybdate and antimony potassium tartrate (catalyst) under acidic conditions to form a 12-molybdophosphoric acid complex (Aquakem Labmedics, 2006; ALS, 2016). The complex was then reduced with ascorbic acid to form a blue heteropoly compound. The absorbance of this compound was measured spectrophotometrically at a wavelength of 880 nm. Ammonia (NH_3^-) reacted with hypochlorite ions generated by the alkaline hydrolysis of sodium dichloroisocyanurate to form monochloramine. This was then reacted with salicylate ions in the presence of sodium nitroprusside at pH 12.6 to form a blue compound. The absorbance of this compound was measured spectrophotometrically at 660 nm.

RESULTS AND DISCUSSION

Effect of digestion acid type on the recovery of metals

The choice of acid or acid-mixture is crucial since it controls the effectiveness of the digestion process. Concentrated hydrochloric and nitric acids were used as pure or in ratios of 3:1 and 1:3 to digest the water samples spiked with a concentration of 0.50 mg/L. The percentage recoveries for the hotplate digestion ranged from 78–117%, 74–111%, 57–102% and 88–116% for 3:1 (HNO_3:HCl), 1:3 (HNO_3:HCl), HCl and HNO_3, respectively (Fig. 2). The microwave-assisted digestion yielded recoveries ranging from 62–95%, 67–111%, 66–113% and 83–103% for 3:1 (HNO_3: HCl), 1:3 (HNO_3: HCl), HCl and HNO_3 respectively (Fig. 3). The concentrated HNO_3 provided recoveries above 80% for all metals in both methods and hence was chosen as the most suitable. This could be due to the good ability of HNO_3 to extract a wide variety of metal salts, while HCl is suitable for metals in the form of carbonates, phosphates, borates, sulfides, and some oxides. Also, metals in the waste matrix tend to form soluble metal salts when subjected to oxidative acid digestion reactions (Das and Ting, 2017).
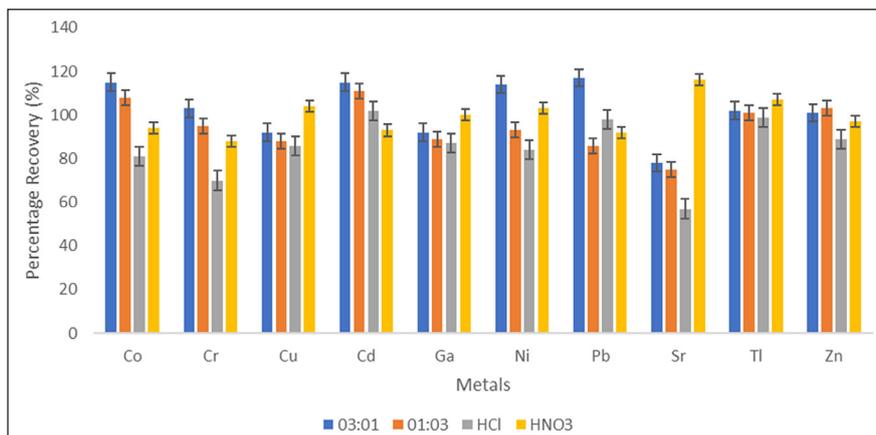
Figure 2. Digestion acid combinations for metal recovery using hotplate digestion
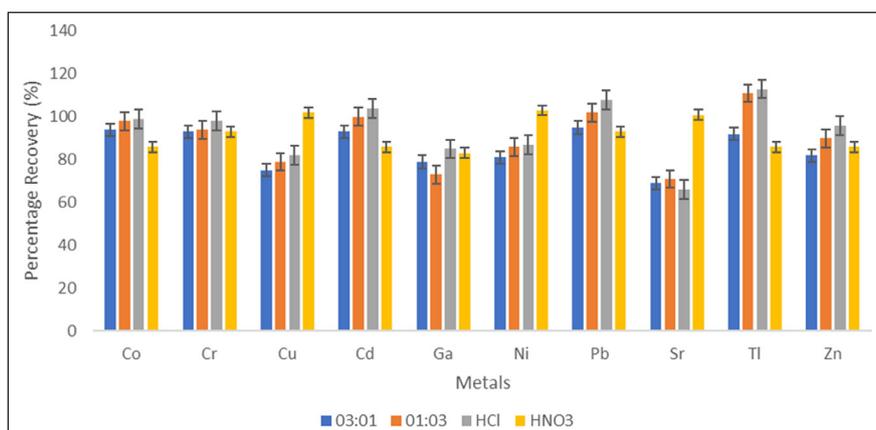
Figure 3. Digestion acid combinations for metal recovery using microwave-assisted digestion
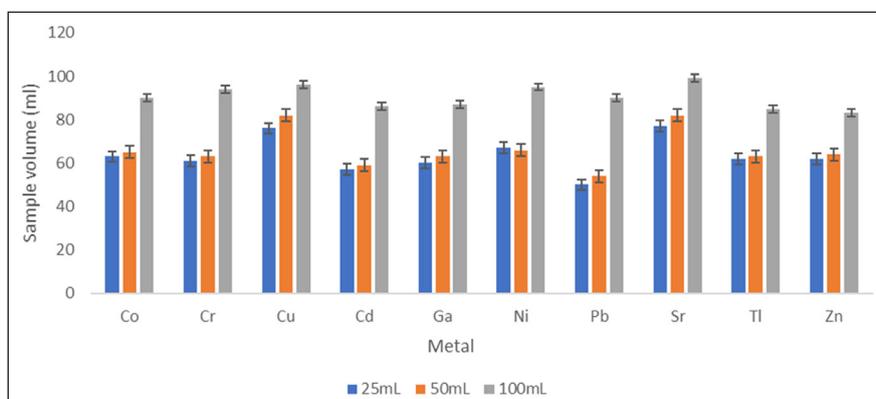
Figure 4. Effect of sample volume on metal recovery

Effect of sample volume on the recovery of heavy metals in hotplate digestion

The effect of sample volume was investigated using 25, 50, and 100 mL of tap water samples. The results showed an increase in all metal recoveries with an increase in sample volume, with recoveries ranging from 83–99% for 100 mL volume (Fig. 4). This could be due to the fact that increasing the sample volume also increases the amount of metals available for digestion and ultimately the concentration recovered in the digestion solvent. Also, the digestion process for large sample volumes takes longer, and this may improve the concentration of metals recovered due to increased contact time. The statistical analysis also confirmed that the mean recovery result for 100 mL is significantly different at the 5% level from that for 25- and 50-mL sample volume (Table A1).

The 100 mL sample was then taken as the optimum volume for further analysis.

Recovery of metals from different water matrices

The tap, river, and wastewater matrices were spiked with a 0.50 mg/L metal mixture, digested, analysed, and the percentage recoveries calculated. There was no trend in metal recoveries from all water samples which indicated that the recoveries are independent of the sample matrix. The recoveries were found to be within an acceptable range of 72–119% (depicted in Fig. 5a–d). Total recoverable metals were higher than the total dissolved metals for both digestion methods. This is expected since the total recoverable determination takes into consideration both the suspended and dissolved metal concentrations.
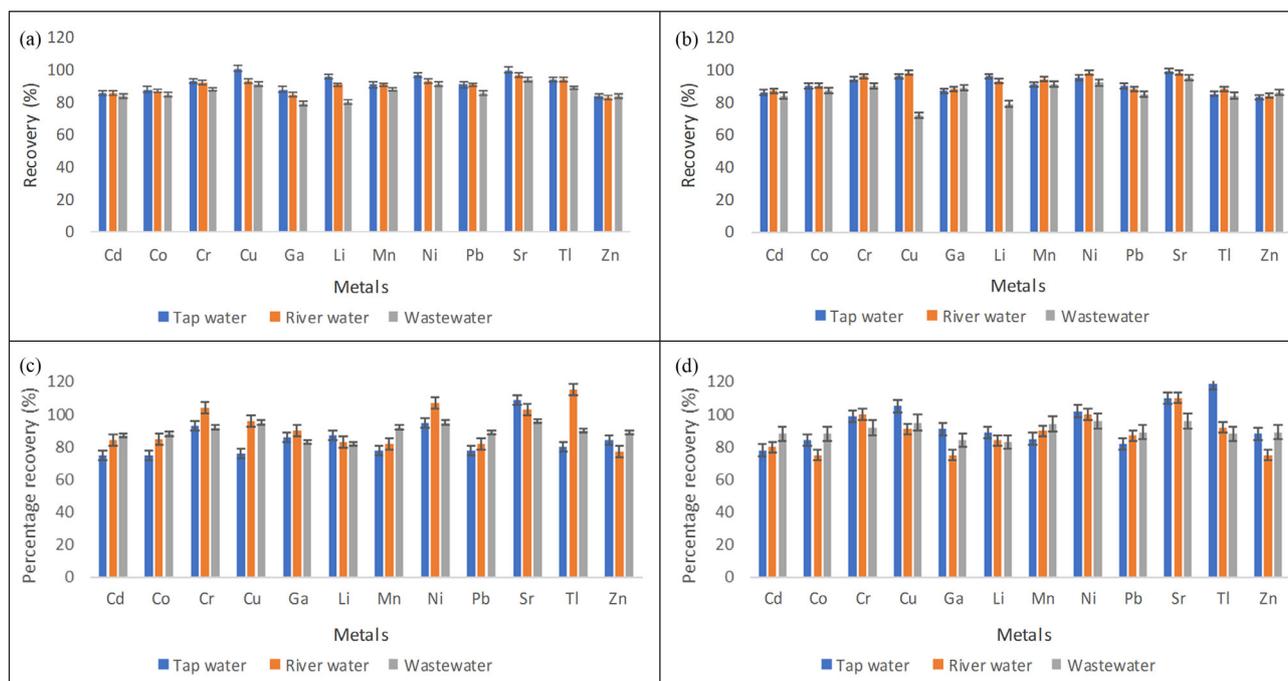
Figure 5. The effect of different water matrices on the total (a) and dissolved (b) metal recovery using hotplate digestion; and total (c) and dissolved (d) metal recovery using microwave-assisted digestion.

However, it was also observed that for some metals the total dissolved recoveries were higher, and this could be due to the sample reduction step in the total recoverable determination where the analyte is lost via evaporation during the heating process (Sastre et al., 2002). A *t*-test showed that the mean recoveries were not significantly different at the 5% level (Table A2).

Effect of spiking concentration on metal recovery

The effect of sample spiking concentration on total recoverable and total dissolved metals for the certified reference material was investigated at 0.10, 0.50, and 1.00 mg/L spike levels. There was no trend observed in the percentage recoveries for the different spiking concentrations therefore it can be reasoned that the recoveries are independent of the sample spiking concentration (Figs 6 and 7). A t-test confirmed that the results were not significantly different at the 5% level (Tables A3, A4, A5).

Physicochemical properties of water samples

Dissolved oxygen (DO), total dissolved solids (TDS), temperature, pH, conductivity, and salinity were measured before the determination of metal concentrations (Table 2). The temperature of tap and river water ranged from 17.4–22.6°C and 17.1–23.2°C, respectively, while for wastewater it ranged from 13.2–24.0°C. Studies have shown that an increase in temperature can result in higher maximum sorption of metals by minerals; however, the average dissolved metal concentrations showed no dependence on temperature at 4–25°C (Huang et al., 2017). A study conducted by Li et al. (2013) showed that Pb concentrations increased with increasing temperature (15–35°C). However, no significant concentration variation was observed. It was also observed that Cd was only detected at temperatures of 30 and 35°C. This is because the oxidiz-able fraction of the metal is transformed easily in chemical reactions that occur when the temperature is increased (Li et al., 2013).

The pH of the collected tap water ranged from 6.2–6.9, within the WHO recommended range for drinking water (6.5–8.5).

An acidic pH can result in the presence of metals (e.g., Fe, Mn, Cu, Pb, and Zn) in drinking water due to leaching from plumbing systems (Rahmanian et al., 2015). The pH in river and wastewater samples was from 7.2–9.0 and 7.1–7.6, respectively, which is slightly basic, and this could be due to the presence of carbonates, bicarbonates, and hydroxides originating from limestone found in the riverbed (Reeve, 2002). Metal ions can also be converted into poorly soluble forms which tend to adsorb on suspended materials present in slightly basic water if there is a high amount of dissolved oxygen.

The DO levels in tap water ranged from 2.41–3.66 mg/L, in river water from 0.64–2.90 mg/L and in wastewater from 0.33–2.61 mg/L. The presence of organic and or inorganic material in water depletes oxygen. For example, Fe^{2+} can deplete oxygen via oxidation to form Fe^{3+} (Reeve, 2002) and oxidation processes can be a possible explanation for the differences between the DO levels in tap and river water samples. Oxidation processes are used in treatment of drinking water, thus increasing DO levels. Therefore, tap water is expected to have higher DO levels compared to river water since microorganisms will significantly decrease DO (Li et al., 2013). Salinity in wastewater ranged from 0.29–0.64 psu and was higher than that of river water (0.10–0.15 psu) and tap water (0.19–0.44 psu). Conductivity of tap, river and wastewater samples ranged from 187–758 µS, 210–888 µS, and 608–1 312 µS, respectively. The maximum allowable limit of conductivity in water as per the NDWQS guidelines (Rahmanian et al., 2015) is 1 000 µS.

Total dissolved solids (TDS) in tap, river, and wastewater samples were from 106–243 mg/L, 105–163 mg/L and 304–658 mg/L, respectively, which were all below the acceptable limit of 1 000 mg/L in drinking water (WHO, 2004). A high concentration of dissolved solids is usually not considered a health hazard; however, it can produce hard water (the presence of carbonates and bicarbonates) which can affect the physical properties of water. It can also indicate that harmful contaminants such as Fe, Mn, SO_4^{2-}, Br, and As are possibly present in the water (Rahmanian et al., 2015).
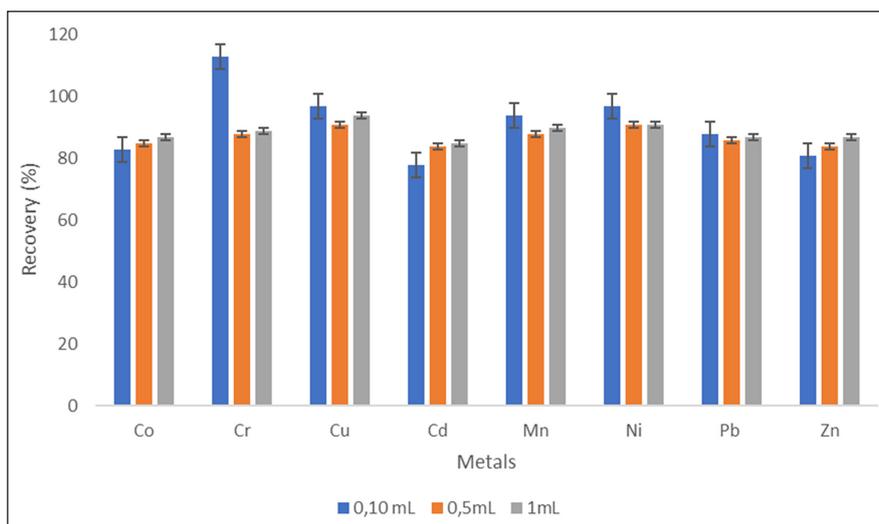
Figure 6. The effect of different spiking concentrations on metal recovery using hotplate digestion
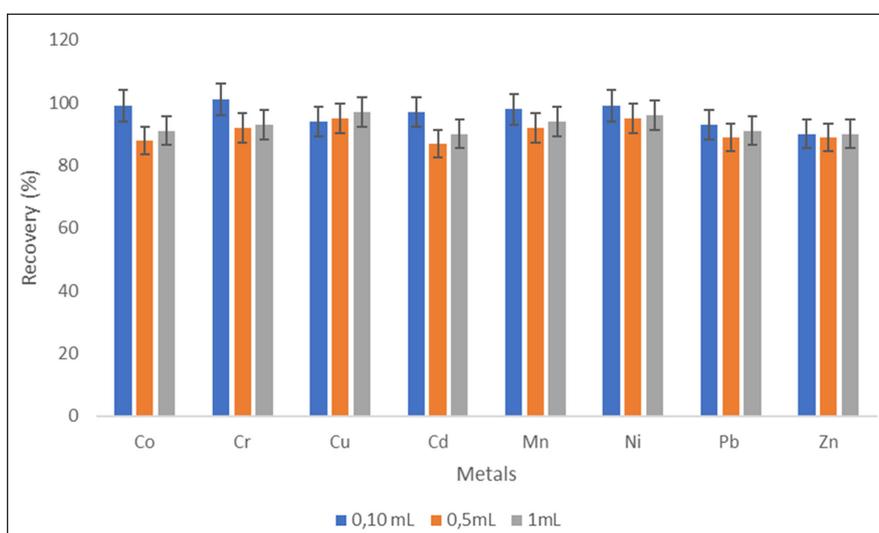
Figure 7. The effect of different spiking concentrations on metal recovery using microwave-assisted digestion

Table 2. Physical properties of water samples

Water source	Sample	DO (mg/L)		Temp (°C)		Salinity (psu)		TDS (mg/L)		pH		Conductivity (µS)	
Tap water	Richmond Crest	3.48		17.4		0.44		168.8		6.75		421	
	Boughton	2.89		19.3		0.35		120.2		6.87		316	
	Woodlands	2.85		22.6		0.28		243		7.39		758	
	Mkhondeni	3.66		20.2		0.19		106		7.34		187	
	Scottsville	2.41		18.8		0.33		206.4		6.21		229	
River water	Camps Drift	2.66		17.1		0.15		163		8.01		328	
	College Road	2.90		23.2		0.10		112		9.01		223	
	YMCA	2.50		17.5		0.10		108		7.98		212	
	Wood House	1.39		17.2		0.10		105		7.59		210	
	Bishopstowe	1.29		22.1		0.15		163		7.25		325	
Wastewater		Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
	Amanzimtoti	0.39	1.56	14.0	18.5	0.59	0.46	623	475	7.12	7.81	1241	945
	Northern	0.48	2.61	15.1	13.2	0.40	0.32	427	339	7.27	7.46	858	675
	Umhlathuzana (MR)	0.33	2.30	17.6	24.0	0.64	0.34	658	352	7.23	7.62	1312	707
	Umhlathuzana (SC)	0.56		14.9		0.29		304		7.05		608	

Determination of metals in wastewater

There was no trend observed between total recoverable and total dissolved metal concentrations in wastewater (Table 3). Co and Li concentrations were found to be higher in influent samples, while they were either below quantification or detection limit in the corresponding effluent samples, indicating their partial removal by the WWTPs. Mn was present in all sludge samples (192–785 µg/L) and higher concentrations were observed for total recoverable than total dissolved Mn. This could be due to the fact that liquid sludge contains some solid particles which can increase the adsorption of Mn and, since total recoverable determination includes dissolved and suspended metals, high concentrations are expected (Addo-Bediako et al., 2018). Ni was only quantified at the Amanzimtoti WWTP influent for total recoverable and total dissolved (118.9 and 235 µg/L). It was below the quantification limit in the effluent and other samples – an indication of efficient removal of Ni at the Amanzimtoti WWTP. Pb, Sr, and Zn concentrations were quantified in all waste and corresponding river water samples (where WWTPs discharge), and were found to be below the maximum permissible limits, with the exception of Pb. The highest Pb concentration was found at the Northern River WWTP for both total recoverable and dissolved determinations. Amanzimtoti WWTP had higher Zn concentrations in the effluent for total dissolved determination. This might be due to particulate Zn in the influent being transferred to the aqueous phase in aeration tanks used in the WWTPs. Also, a higher amount of metals in the activated sludge may be transferred to the aqueous phase in aeration tanks which might increase the amount of Zn present in the effluent (Yamagata et al., 2010). Co was detected in Amanzimtoti influent and sludge at 37.4 µg/L and 28.6 µg/L, respectively, as well as in Northern Works influent and sludge at 37.6 µg/L and 40.7 µg/L, respectively. Li was detected in Amanzimtoti influent and sludge at 13.9 µg/L and 20.3 µg/L, respectively, and in Northern Works sludge (17.6 µg/L) and Umhlathuzana influent (7.3 µg/L). Lastly, Cd, Cr, Cu, Co, Li, Ni, and Tl were below detection or quantification limits.

Determination of metals from tap and river water

The average concentrations observed for total recoverable metals were much higher than for total dissolved metals in tap and river water (Table 4 and 5). This was expected since the total recoverable metal concentrations consider the soluble and insoluble metals (unfiltered samples) whilst the total dissolved metal concentration only considers the soluble metals as particulates (insoluble) are removed by filtration (USEPA, 1994). However, some metals had higher total dissolved compared to total recoverable concentrations, especially when using microwave digestion. This could be due to the microwave method being a closed-system digestion, which, apart from a considerable reduction in digestion time, also results in minimal sample contamination and loss of volatile metals such as As, Hg, and Cr (Sastre et al., 2002). In tap water, Li concentrations were approximately the same (4.9–5.5 µg/L) for all samples for both digestion methods, whereas for river water, Li was only quantified in Woodhouse River water (34.5 µg/L) using the microwave digestion method. There is no maximum permissible limit set for Li in drinking water; however, the obtained values were below the oral reference dosage which is 700 µg/L (USEPA, 2003); hence the analysed tap water can be assumed to be safe for consumption. Li has also been detected in tap water at 20–160 µg/L and 0.7–59.0 µg/L from Texas and Japan, respectively (Ohgami et al., 2009), and the maximum concentrations were higher than those obtained in this work. The highest concentration obtained for Sr was 90.8 µg/L (Richmond Crest) which is lower than that reported in drinking water from China (1 690.0 µg/L) by Zhang et al. (2018).

The highest concentration of Zn (142.3 µg/L) was observed in the Scottsville tap water sample. The presence of Zn (147.6–307.1 µg/L) in drinking water from Jordan has also been reported (Massadeh et al., 2020), at higher concentrations than those reported here, but still below the permissible limits. Pb was the only metal found in all tap water samples (59.2–155.1 µg/L) that was present above the permissible limit of 50.0 µg/L. This indicates that tap water from all the sampling areas is not safe for human consumption, as Pb is one of the most toxic metals, which can lead to permanent damage to the nervous system, brain, and kidneys in humans and animals. Pb has various industrial applications which can result in lead contamination of water supplies through indirect pathways. It is commonly found in batteries, water distribution piping, and paints, and occurs as an organic compound, alkyl lead, in gasoline. The presence of Pb in tap water can be from the dissolution of household plumbing systems where the pipes, solder, fittings, or service connections to homes contain Pb (Mebrahtu et al. 2011; Mehdizadehtapeh et al., 2017; Fajri et al., 2023). The dissolution of Pb is generally increased in soft water, i.e., water containing low levels of calcium carbonate (SAWQG, 1996). These results agree with those reported by Massadeh et al. (2020), where concentrations of Pb above permissible limits were observed in drinking water from Jordan (7.7–60.6 µg/L), suggesting that Pb contamination of drinking water is a prevalent global problem. Cu and Co were not found in tap water samples, while Cr, Tl, Mn, Ni, and Cd were either below detection or quantification limits. Even though the concentration levels for all other heavy metals in this study are within the permissible limits, the high Pb concentration needs to be continuously monitored to ensure that tap water is safe for human consumption, with appropriate treatment processes of coagulation with alum, ferric salts or lime thereafter followed by settlement and filtration (SAQGW, 1996).

Table 3. Average total recoverable (TR) and total dissolved (TD) metal concentrations (µg L^{-1}) obtained in wastewater, river water, and sludge samples using microwave-assisted digestion, $n = 3$

Metal	Amanzimtoti								Umhlathuzana										Northern Works							
	TR				TD				TR					TD					TR				TD			
	Inf	Eff	SG	RV	Inf	Eff	SG	RV	Inf 1	Inf 2	Eff	SG	RV	Inf 1	Inf 2	Eff	SG	RV	Inf	Eff	SG	RV	Inf	Eff	SG	RV
Mn	95.8 ±0.2	0 ±0.01	396 ±0.4	bdl	115 ±0.7	87.0 ±0.1	363 ±0.6	bdl	107 ±0.2	bql	101 ±0.9	200 ±1.2	Bdl	102 ±1.0	bql	bql	192 ±0.8	bql	bql	bql	785 ±2.4	bql	bql	Bql	715 ±2.1	bql
Pb	bql	bql	59.1 ±0.2	45.8 ±0.1	40.4 ±0.08	18.2 ±0.05	bql	29.5 ±0.04	bdl	bql	bdl	bdl	28.3 ±0.08	23.2 ±0.03	bdl	40.3 ±0.07	bql	45.6 ±0.1	225 ±1.2	bdl	bdl	34.4 ±0.1	bdl	54.7 ±0.1	bql	63.9 ±0.1
Sr	233 ±1.2	98.5 ±0.8	117 ±1.0	465 ±2	96.5 ±0.9	59.0 ±0.5	88.2 ±0.3	462 ±2.1	56.9 ±1.8	35.4 ±0.8	30.6 ±0.5	78.1 ±1	69.2 ±1.8	61.4 ±1.5	30.0 ±0.4	38.6 ±0.7	87.6 ±1.7	70.9 ±1.2	50.1 ±0.9	41.6 ±0.5	83.7 ±1.7	437 ±2.8	82.6 ±1.3	81.9 ±1.6	92.1 ±2	416 ±3.1
Zn	302 ±3.2	72.4 ±1	58.6 ±0.7	16.0 ±0.2	79.0 ±1.2	151 ±2	21.9 ±0.4	15.7 ±0.2	37.3 ±0.6	34.3 ±0.4	129 ±2.3	49.1 ±1.1	56.7 ±1	114 ±1.8	93.6 ±1	62.5 ±0.9	90.9 ±1	129 ±1.6	125 ±2	49.2 ±1	102 ±2.4	332 ±3.1	223 ±3	138 ±2.0	9.7 ±0.1	339 ±2.5

bdl – below detection limit, bql – below quantification limit, inf – influent, eff – effluent, SG – sludge, RV – River, Inf 1 – Marian Ridge, Inf 2 – Shallcross

Table 4. Average concentrations (µg/L) for total recoverable (TR), total dissolved (TD) metals in tap water from the hotplate and microwave digestion methods and permissible limits (µg/L: WHO, 2004; USEPA, 2003), *n* = 3

Metal	Hotplate digestion										Microwave-assisted digestion									
	Sampling site										Sampling site									
	RC		SV		MN		WL		BT		RC		SV		MN		WL		BT	
	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD
Li	5.4 ±0.09	5.1 ±0.08	5.0 ±0.08	5.0 ±0.08	5.0 ±0.08	5.0 ±0.08	5.0 ±0.08	5.4 ±0.1	5.0 ±0.09	4.9 ±0.06	5.3 ±0.09	5.3 ±0.09	4.9 ±0.04	4.9 ±0.07	5.1 ±0.08	4.9 ±0.06	5.0 ±0.08	5.0 ±0.08	5.0 ±0.08	5.0 ±0.08
Pb	69.3 ±0.09	78.6 ±0.09	59.2 ±0.07	62.5 ±0.09	79.2 ±0.1	61.1 ±0.09	116 ±0.2	82.1 ±0.1	75.0 ±0.09	62.0 ±0.08	84.7 ±0.1	62.0 ±0.09	74.1 ±0.1	58.2 ±0.09	155 ±0.4	78.9 ±0.09	64.0 ±0.08	58.6 ±0.05	72.0 ±0.09	91.6 ±0.1
Sr	39.1 ±0.3	90.8 ±0.8	33.4 ±0.1	17.2 ±0.09	38.9 ±0.1	17.2 ±0.06	36.4 ±0.09	19.4 ±0.04	37.8 ±0.09	18.2 ±0.07	46.5 ±0.6	32.1 ±0.09	41.1 ±0.1	33.9 ±0.08	40.1 ±0.09	34.8 ±0.06	37.1 ±0.05	33.1 ±0.07	36.9 ±0.09	36.3 ±0.09
Zn	23.5 ±0.1	12.5 ±0.06	114 ±0.2	58.9 ±0.2	37.0 ±0.1	19.8 ±0.07	50.2 ±0.1	121 ±0.3	65.5 ±0.1	20.0 ±0.09	31.5 ±0.09	11.5 ±0.02	143 ±0.5	118 ±0.2	111 ±0.2	28.5 ±0.07	46.8 ±0.09	28.3 ±0.08	33.7 ±0.09	40.4 ±0.09

bdl – below detection limit, bql – below quantification limit, BS – Bishopstowe, CD – Camps Drift, CR – College Road, WH – Woodhouse, RC – Richmond crest, SV – Scottsville, MN – Mkhondeni, WL – Woodlands, BT – Boughton

Table 5. Average concentrations (µg/L) for total recoverable (TR) and total dissolved (TD) metals in river water from the hotplate and microwave digestion methods and permissible limits (µg/L: WHO, 2004; USEPA, 2003), *n* = 3

Metal	Sampling site																			
	BS		CR		CD		WH		YMCA		BS		CR		CD		WH		YMCA	
	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR	TD	TR
Ga	Bql	bql	bql	bql	Bql	bql	bql	bql	bql	Bql	bdl	bql	bdl	bql	bdl	bql	bdl	bql	bdl	bql
Pb	30.1 ±0.2	36.4 ±0.2	30.6 ±0.1	30.6 ±0.1	30.1 ±0.1	32.5 ±0.1	43.7 ±0.4	30.9 ±0.1	34.4 ±0.2	52.3 ±0.4	27.8 ±0.09	32.4 ±0.1	51.7 ±0.3	51.8 ±0.2	27.1 ±0.08	40.4 ±0.2	42.6 ±0.2	35.3 ±0.1	42.4 ±0.07	27.0 ±0.07
Sr	38.9 ±0.1	73.3 ±0.6	40.5 ±0.1	69.1 ±0.6	65.2 ±0.5	120 ±0.9	42.7 ±0.2	77.2 ±0.7	39.7 ±0.1	76.0 ±0.5	70.3 ±0.4	66.2 ±0.5	86.7 ±0.6	72.1 ±0.5	115.3 ±0.8	131.4 ±0.9	75.4 ±0.5	131.8 ±0.8	70.3 ±0.5	71.4 ±0.5
Zn	15.5 ±0.09	5.9 ±0.05	bdl	9.7 ±0.07	6.8 ±0.07	bdl	bdl	17.2 ±0.09	5.9 ±0.07	13.4 ±0.07	32.2 ±0.1	8.8 ±0.07	48.7 ±0.2	11.4 ±0.08	9.0 ±0.07	23.9 ±0.09	12.0 ±0.08	58.4 ±0.4	12.2 ±0.09	bdl

bdl – below detection limit, bql – below quantification limit, BS – Bishopstowe, CD – Camps Drift, CR – College Road, WH – Woodhouse, RC – Richmond crest, SV – Scottsville, MN – Mkhondeni, WL – Woodlands, BT – Boughton

In river water, Zn was present in most samples, and was highest in the Woodhouse sample (58.4 µg/L), but was lower than the concentration (200.0 µg/L) recorded by Addo-Bediako et al. (2018) in the Steelpoort River in Limpopo Province. The increased concentration may be due to the sorption of Zn by hydrous metal oxides, clay minerals and organic material commonly found in river systems. However, Zn can be toxic to organisms when present in higher concentrations (Mebrahtu et al., 2011). The presence of Zn could also be due to pesticide and fertilizer contamination through agricultural runoff (Oguzie et al., 2010). Sr and Pb concentrations were detected in all samples and were below the permissible limits, with the exception of Pb at YMCA and College Road (Table 5). The presence of Sr in water could be due to the weathering of natural rocks as well as the direct discharge of wastewater into rivers. The possible sources of high Pb concentrations in river water could be exhaust emissions from motor vehicles that can make their way into river systems. This can have adverse effects on the surrounding environment such as inhibiting the growth of plants and affecting the central nervous system of humans upon consumption (Mebrahtu et al., 2011). The maximum concentration of Pb (51.8 µg/L) obtained in this work is lower than that reported by Olujimi et al. (2018) for river water from Gauteng (86.73 µg/L); however, both studies recorded Pb levels above the permissible limits. The concentrations of Cd, Cr, Mn, Ni, Ga, and Tl were found to be below the detection or quantification limits in river water samples.

In general, it was observed that microwave-assisted digestion was more sensitive as higher concentrations of metals were detected and quantified in all samples. Some metal concentrations quantified using the microwave-assisted method were either below the detection or quantification limits for the hotplate method.

For both digestion methods, statistical analysis showed that the concentrations obtained were not significantly different (Table A6). In addition to the *t*-test, a one-way ANOVA was conducted on the two digestion methods which revealed that there is no significant difference between the methods as $F_{critical} > F_{value}$ with $p \geq 0.05$ (Table A7). It can be concluded that the hotplate method can be recommended for daily routine analysis as it is a cheaper technique compared to microwave-assisted digestion. The reason for the differing concentrations of heavy metals in water samples is that despite the assumption that applications are the same in nearly all countries, consumption patterns for chemicals may be different. For instance, some applications that may have been phased out in some countries may be widely used in other countries resulting in the presence or absence of certain heavy metals in water systems (Olujimi et al., 2012).

There were some inconsistencies concerning total dissolved metals being higher than total recoverable metals. These non-correlations may be subjected to sample matrix interferences, by the loss of sample volume during the digestion process, sample contamination during analysis, and high volatility of metals in the presence of high temperatures (Sastre et al., 2002; Lomonte et al., 2008).

Metal removal efficiency of WWTPs

The removal efficiency (%) for heavy metals in WWTPs was calculated using Eq. 1:

$$\text{Removal efficiency} = \frac{C_{influent} - C_{effluent}}{C_{influent}} \times 100 \quad (1)$$

where: $C_{influent}$ and $C_{effluent}$ are the concentrations obtained in the raw influent and final effluent, respectively.

Cd and Li were completely removed from the Amanzimtoti WWTP. Also, Mn was completely removed at Umhlathuzana, while −106% and 3.9% were removed at Amanzimtoti and Northern Works, respectively. Pb removal was 25%, −125%, and 14.7%; Sr removal was 37.6%, 55.4%, and −20.3%; Zn removal was 07.9%, −9.1% and −30.1% at Amanzimtoti, Umhlathuzana and Northern, respectively. Zn showed negative removal in all WWTPs which indicated its high persistence within the wastewater treatment plants. A study conducted in Japan by Yamagata et al. (2010) revealed that Zn on adsorbed particulates could be easily removed; however, there was difficulty in removal of dissolved Zn in the influent during the activated sludge process. Amanzimtoti achieved better removal efficiency for most of the metals compared to Umhlathuzana and Northern Works. These results indicate that the WWTPs contribute to heavy metal pollution of the rivers they discharge their effluents into.

Anion concentration

Phosphates were detected in all water samples (Table 6). The presence of some phosphates in water is natural as it is an essential nutrient; however, agricultural (over-fertilization) and industrial resources tend to increase the phosphates in natural surface water which may result in eutrophication and excessive algal blooms (Altundag et al., 2019). The concentration of phosphates was found to be lower in the effluent compared to the corresponding influent which could be due to the treatment processes applied in the plant and also adsorption on the sludge (El-Nahhal et al., 2014). The highest phosphate concentration was found in sludge samples from Amanzimtoti WWTP (175 mg/L), possibly because of the solubility and pH effect, as low pH values permit the adsorption of phosphate on sludge. Sludge samples had a pH of 7.36 ± 0.03; hence, phosphates were detected as this pH

influenced them to strongly bind to the sludge. Also, phosphoric acid is a weak acid with three dissociations; hence the phosphate levels observed in the sludge are those found in a neutral pH. However, more phosphates are expected to be found at a more acidic pH (El-Nahhal et al., 2014). The highest concentration of phosphates in river water was observed in Amanzimtoti River (13.0 mg/L), which was than that reported for the Sakarya River in Turkey (2.72 mg/L) (Altundag et al., 2019).

Chloride concentrations were found to be below the maximum acceptable values, except in the Amanzimtoti and Northern River water samples. Scottsville tap water had the highest chloride level of all tap water samples (8.12 mg/L), but this was still below the maximum allowable limit. Chlorides are expected to be present in tap water since chlorination is used in water treatment. In river water, the highest concentration above the maximum limit was found in Amanzimtoti (3 064.54 mg/L), which was higher than that observed at the Sakarya River in Turkey (78.52 mg/L) (Altundag et al., 2019). The chloride concentration in the river water could be due to natural sources such as weathering of rocks and concentrations can increase because of evaporation.

The highest nitrate concentration in river water was observed at Bishopstowe (6.42 mg/L), but this value is lower than that observed in the Sakarya River (920 mg/L) by Altundag et al. (2019). Nitrates can reach surface waters from agricultural activity (fertilizers), oxidation of nitrogenous wastes, human and animal excreta. Scottsville tap water recorded the highest nitrate concentration for all tap water samples. Nitrates in tap water may be due to nitrite being formed chemically in distribution pipes by *Nitrosomonas* bacteria during the stagnation of nitrate-containing and oxygen-poor drinking water in galvanized pipes. Another reason could be when chlorination (not a well-controlled process)

Table 6. Concentrations of anions (mg/L) in water samples

Source	Sample location	Anion				
		PO_4^{3-}	Cl^-	NO_3^-	NH_3	SO_4^{2-}
Tap water	Richmond Crest	3.00	0.50	0.03	23.51	–
	Mkhondeni	0.09	7.68	0.42	0.49	0.28
	Boughton	3.00	0.40	0.00	8.65	–
	Scottsville	0.08	8.12	0.71	0.26	0.25
River water	College Road	3.00	0.80	0.18	3.39	–
	Woodhouse	4.00	0.90	0.00	3.91	–
	YMCA	3.00	0.80	0.00	3.84	–
	Bishopstowe	1.00	47.17	6.42	0.24	39.15
	Camps Drift	0.26	40.53	3.81	0.34	16.01
	Mbokodweni	1.60	3 064.54	3.20	0.02	437.80
	Mgeni	0.27	1 454.78	2.17	0.30	292.47
	Umhlathuzana	13.00	2.8	1.74	3.60	-
Wastewater	Amanzimtoti infl.	11.19	215.13	0.32	2.85	49.29
	Amanzimtoti effl.	7.91	108.10	9.21	0.01	53.89
	Amanzimtoti sludge	175.67	105.62	39.57	158.44	35.72
	Northern infl.	5.61	107.98	0.25	4.66	11.87
	Northern effl.	3.43	103.25	32.77	0.08	59.01
	Northern sludge	126.26	96.40	3.79	44.05	66.39
	Umhlathuzana MR infl.	78.00	3.4	0.00	148.29	–
	Umhlathuzana SC infl.	22.00	2.3	1.72	139.44	–
	Umhlathuzana effl.	24.00	3.5	2.26	9.94	–
Acceptable limits (USEPA, 2003; Koch, 1984; WHO, 2004)		–	250	45 or 50	–	250

– not analysed
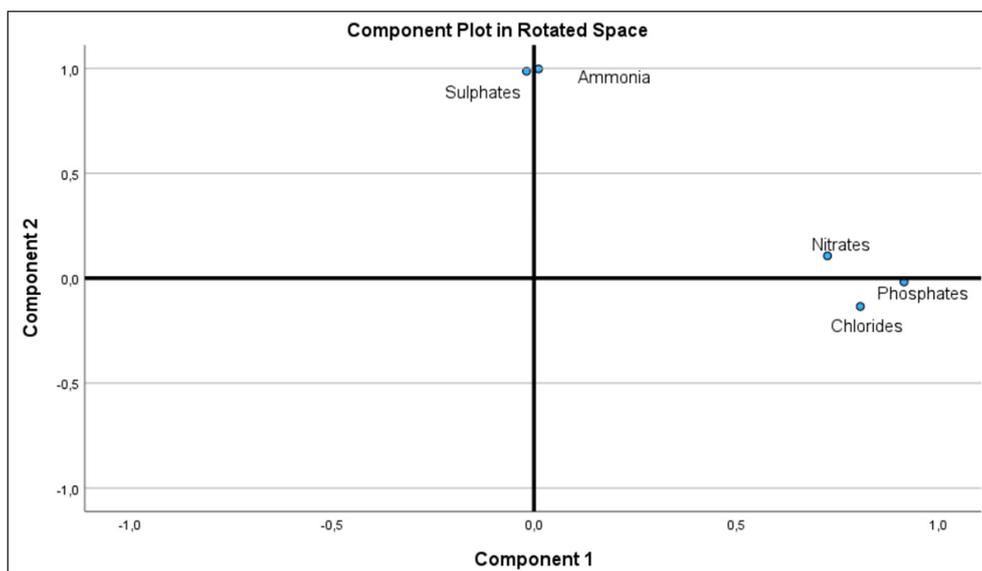
Figure 8. Rotated component matrix for anions in different water matrices

is used as a disinfectant thus increasing the nitrate concentration in the tap water (Koch, 1984). The reduction of nitrate to nitrite gives rise to its toxicity in humans and high concentrations can cause the oxidation of haemoglobin (Hb) to methaemoglobin (metHb), which is unable to transport oxygen to tissues (Koch, 1984). In wastewater, Amanzimtoti WWTP sludge had the highest concentration of nitrates (39.57 mg/L) while the influent had the lowest concentration (0.32 mg/L). The Northern Works and Umhlathuzana also produced high concentrations in the effluent compared to the influent, though still below acceptable levels. The high concentration of nitrates in effluent compared to influent could be due to the re-concentration of cations and anions which results in the conversion of ammonium hydroxide to nitrates in the presence of oxygen and nitrifying bacteria within the WWTP (El-Nahhal et al., 2014).

Ammonia levels were found to be the highest in Richmond Crest tap water (23.51 mg/L), while the highest concentration of ammonia in river water was observed at Woodhouse (3.91 mg/L). Ammonia can have toxic effects on humans when consumed in large amounts resulting in compromised capacity to detoxify. High levels of ammonia can also lead to toxic build-up in tissues and blood in aquatic organisms. The main source of ammonia is human faeces containing a high protein fraction due to high consumption of protein (El-Nahhal et al., 2014). All WWTPs successfully removed the ammonia from the influent water resulting in low concentrations in the effluent and river water samples. The high concentrations of ammonia in influent could be due to fertilizers and other agricultural products containing ammonia (Altundag et al., 2019).

The highest concentrations of sulfates above permissible limits were observed in the river samples for both Amanzimtoti (437.80 mg/L) and Northern Works (292.47 mg/L). Sulphate is the most common anion after bicarbonate and chloride (Altundag et al., 2019). Sulphates occur naturally in minerals such as barite, epsomite, and gypsum, and this can contribute to the sulphate content in drinking water. Other sources include fertilized agricultural lands and sewage treatment plants (Altundag et al., 2019). The high concentration of sulphates in the water samples may also be due to the high solubility of sulphates in river water which is not pH dependent(El-Nahhal et al., 2014; Jing et al., 2013). Although high sulphate concentrations can result in dehydration, it has been reported that humans can adapt to high sulphate levels with time (WHO, 2004).

Table 7. PCA for anions in different water matrices component plot in rotated space

Rotated component matrix		
Anion	Component 1	Component 2
Phosphates	0.919	
Chlorides	0.829	
Nitrate	0.709	
Ammonia		0.995
Sulphates		0.989

The common sources of the analysed anions were assessed by performing a principal component analysis (PCA) on the results obtained (Table 7). In Component 1, phosphates, chlorides, and nitrates are closely associated with each other; this implies that they may originate from the same source, which could be agricultural fertilizers. Similarly, ammonia and sulphate are closely associated with each other. This is evident from the component plot in the rotated space (Fig. 8). Both ammonia and sulphates are key ingredients in soil fertilizer, e.g. ammonium sulphate, which is an inorganic salt, is commonly present in fertilizers and also has various commercial uses (Altundag et al., 2019).

CONCLUSION

This study focused on the development of two commonly used digestion methods: microwave-assisted and hotplate digestion. The parameters investigated included digestion acid type, acid combinations, sample volume, and spiking concentrations. Concentrated nitric acid (55% v/v) and a sample volume of 100 mL proved to be optimal conditions for sample digestion. Both digestion methods proved to be reliable; however, hotplate digestion was recommended for daily analysis as it is a more accessible and cheaper method. Microwave-assisted digestion provided evident advantages as a sample digestion method with high metal recovery. Total and dissolved metals were quantified using the ICP−OES. All metals (except Pb) and anions (except for chlorides and sulphates in Amanzimtoti and Northern rivers) were below the maximum permissible limits. PCA analysis grouped phosphates, chloride and nitrates (anions) indicating that they are potentially originating from the same source while sulphates and ammonia were also grouped suggesting that they could be from the

same source. Lead in particular was present in tap water at levels above the legislative limit for drinking water. The possible sources included water distribution piping in households, paints, and other organic compounds in gasoline through indirect pathways. In some instances, total dissolved metals were higher than total recoverable metals. It was observed that WWTPs also contribute towards the presence of metals in rivers. The efficiency of the wastewater treatment plants was calculated by percentage removal. This indicated that treatment processes require improvement or perhaps new processes to be implemented to remove these pollutants before discharge into river systems, in order to safeguard human health on consumption and to ensure clean freshwater resources.

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REFERENCES

ADDO-BEDIAKO A, MATLOU K and MAKUSHU E (2018) Heavy metal concentrations in water and sediment of the Steelpoort River, Olifants River system, South Africa. *Afr. J. Aquat. Sci.* **43** (4) 413–416. https://doi.org/10.2989/16085914.2018.1524745

ALTUNDAG H, AGAR S, ALTINTIG E, ATES A and SIVRIKAYA S (2019) Use of ion chromatography method on the determination of some anions in the water collected from Sakarya, Turkey. *J. Chem. Metrol.* **13** (1) 14–20. https://doi.org/10.25135/jcm.26.19.03.1221

ATLAS A, USMAN K, REHMAN H, KHUDADAD S, MUNAWAR A, RAB A, KHAN MI, GUL M and PERVAIZ M (2017) Analysis of heavy metals in River Kabul at Sardaryab Khyber Pakhtunkhwa, Pakistan. *J. Entomol. Zool. Stud.* **5** (6) 14–16.

AUSTRALIAN LABORATORY SERVICES (2016) Environmental Method Statements. https://www.alsenvironmental.co.uk/client-services/method_statements (Accessed December 2023).

DAS S and TING YP (2017) Evaluation of wet digestion methods for quantification of metal content in electronic scrap material. *Resources* **6** (64) 1–16. https://doi.org/10.3390/resources6040064

EL-NAHHAL IY, AL-NAJAR H and EL-NAHHAL Y (2014) Physicochemical properties of sewage sludge from Gaza. *Int. J. Geosci.* **5** (6) 586–594. https://doi.org/10.4236/ijg.2014.56053

FAJRI PY, PUTRI NE, AGUSTINA A and DESMINARTI S (2023) Analysis of heavy metals on various refilled drinking water depots circulated in Limapuluh Kota Regency, West Sumatera Province by inductively coupled plasma (ICP) methods. *Earth Environ. Sci.* **1182** 012065 https://doi.org/10.1088/1755-1315/1182/1/012065

HUANG Y, ZHANG D, XU Z, YUAN S, LI Y and WANG L (2017) Effect of overlying water pH, dissolved oxygen, and temperature on heavy metal release from river sediments under laboratory conditions. *Arch. Environ. Protect.* **43** (2) 28–36. https://doi.org/10.1515/aep-2017-0014

JAISHANKAR M, TSETEN T, ANBALAGAN N, MATHEW B and BEEREGOWDA K (2014) Toxicity, mechanism, and health effects of some heavy metals. *Interdisc. Toxicol.* **7** (2) 60–72. https://doi.org/10.2478/intox-2014-0009

JING Z, HU Y, NIU Q, LIU Y, LI YY and WANG XC (2013) UASB Performance and electron competition between methane-producing archaea and sulfate-reducing bacteria in treating sulfate-rich wastewater containing ethanol and acetate. *Bioresour. Technol* **137** 349–357. https://doi.org/10.1016/j.biortech.2013.03.137

KOCH R (1984) Guidelines for drinking water quality, Volume I – recommendations. World Health Organization, Geneva. *Acta Hydrochim. Hydrobiol.* **12** (2) 221–223. https://doi.org/10.1002/aheh.19840120217

LEHTONEN J, HASSINEN J, HONKANEN R, KUMAR AA, VISKARI H, KETTUNEN A, PAHIMANOLIS N, PRADEEP T, ROJAS OJ and IKKALA O (2019) Effects of chloride concentration on the water disinfection performance of silver containing nanocellulose-based composites. *Sci. Rep.* **9** 19505. https://doi.org/10.1038/s41598-019-56009-6

LI H, SHI A, LI M and ZHANG X (2013) Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. *J. Chem.* 1–11. https://doi.org/10.1155/2013/434012

MASSADEH A, EL-RJOOB A and GHARAIBEH S (2020) Analysis of selected heavy metals in tap water by inductively coupled plasma-optical emission spectrometry after pre-concentration using chelex-100 ion exchange resin. *Water Air Soil Pollut.* **231** 243. https://doi.org/10.1007/s11270-020-04555-5

MEBRAHTU G and ZERABRUK S (2011) Concentration and health implication of heavy metals in drinking water from urban areas of Tigray Region, Northern Ethiopia. *Momona Ethiop. J. Sci.* **3** (1) 105–121. https://doi.org/10.4314/mejs.v3i1.63689

MEHDIZADEHTAPEH L, TEKINER IH and OZPINAR H (2017) Investigation of heavy metal levels in drinking and well water samples using ICP-MS method. *J. Appl. Food Technol.* **4** (1) 1–7.

OGUZIE FA and OKHAGBUZO GA (2010) Concentrations of heavy metals in effluents discharge downstream of Ikpoba river in Benin City, Nigeria. *Afr. J. Biotechnol.* 9 (3) 319–325.

OHGAMI H, TERAO T, SHIOTSUKI I, ISHII N and IWATA N (2009) Lithium levels in drinking water and risk of suicide. *Brit. J. Psychiat.* **194** 464–465. https://doi.org/10.1192/bjp.bp.108.055798

OLUJIMI O, FATOKI O, ODENDAAL J and OPUTU O (2015) Variability in heavy metal levels in river water receiving effluents in Cape Town, South Africa. *Research and Practices in Water Quality.* IntechOpen, London. https://doi.org/10.5772/59077

OLUJIMI OO, FATOKI OS, ODENDAAL J, DASO AP and OPUTU O (2012) Preliminary investigation into occurrence and removal of arsenic, cadmium, mercury, and zinc in wastewater treatment plants in Cape Town and Stellenbosch. *Pol. J. Environ. Stud.* **21** (6) 1755–1765.

OLOWOYO JO, CHILIZA U, SELALA C and MACHEKA L (2022) Health risk assessment of trace metals in bottled water purchased from various retail stores in Pretoria, South Africa. *Int. J. Environ. Res. Public Health* **19** (22) 15131. https://doi.org/10.3390/ijerph192215131

RAHMANIAN N, ALI S, HOMAYOONFARD M, ALI N, REHAN M, SADEF Y and NIZAMI A (2015) Analysis of physiochemical parameters to evaluate the drinking water quality in the state of Perak, Malaysia. *J. Chem.* **2015** 1–10. https://doi.org/10.1155/2015/716125

REEVE R (2002) *Introduction to Environmental Analysis.* John Wiley & Sons Ltd, Chichester. 56 pp.

SASTRE J, SAHUQUILLO A, VIDAL M and RAURET G (2002) Determination of Cd, Cu, Pb, and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Anal. Chim. Acta* **462** (1) 59–72. https://doi.org/10.1016/S0003-2670(02)00307-0

SMIRNOVA SV, ILIN DV and PLETNEV IV (2021) Extraction and ICP-OES determination of heavy metals using tetrabutylammonium bromide aqueous biphasic system and oleophilic collector. *Talanta* **221** 121485. https://doi.org/10.1016/j.talanta.2020.121485

SOUTH AFRICAN WATER QUALITY GUIDELINES (1996) Volume 1: Domestic Water Use Second Edition.

THERMO SCIENTIFIC (2006) Technical specification Aquakem, Method id ALKBpB http://www.unitylabservices.eu/content/dam/tfs/SDG/CDD/CD.pdf (Accessed December 2023).

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY (2003) US EPA proposes drinking water rules. *Filtration Sep.* **40** (7) 10 pp. https://doi.org/10.1016/s0015-1882(03)00713-4

WORLD HEALTH ORGANIZATION (2004) WHO issues revised drinking water guidelines. *Membr. Technol.* **2004** (11) pp4. https://doi.org/10.1016/s0958-2118(04)00256-3

YAMAGATA H, YOSHIZAWA M and MINAMIYAMA M (2010) Assessment of current status of zinc in wastewater treatment plants to set effluent standards for protecting aquatic organisms in Japan. *Environ. Monit. Assess.* **169** 67–73. https://doi.org/10.1007/s10661-009-1151-y

ZHANG H, ZHOU X, WANG L, WANG W and XU J (2018) Concentrations and potential health risks of strontium in drinking water from Xi'an, Northwest China. *Ecotoxicol. Environ. Saf.* **164** 181–188. https://doi.org/10.1016/j.ecoenv.2018.08.017

APPENDIX

Table A1. Statistical analysis of effect of sample volume on metal recoveries by hotplate method

Statistic	t-test: Two-sample assuming unequal variances					
	25 mL	50 mL	25 mL	100 mL	50 mL	100 mL
Mean	62.33333	64.91667	62.33333	91.58333	64.91667	91.58333
Variance	124.0606	140.2652	124.0606	29.7197	140.2652	29.7197
Observations	12	12	12	12	12	12
Hypothesized mean difference	0		0		0	
Df	22		16		15	
t stat	−0.55043		−8.17083		−7.08523	
P(T ≤ t) one-tail	0.293786		2.11 x 10⁻⁷		1.86 x 10⁻⁶	
t critical one-tail	1.717144		1.745884		1.75305	
P(T ≤ t) two-tail	0.587571		4.21 x 10⁻⁷		3.71 x 10⁻⁶	
t critical two-tail	2.073873		2.119905		2.13145	

Table A2. Statistical analysis of effect of digestion method on metal recoveries: *t*-test assuming unequal variances for the three water matrices

Statistic	Hotplate						Microwave					
	Tap	River	Tap	Waste	River	Waste	Tap	River	Tap	Waste	River	Waste
Mean	93.000	90.636	93.000	86.818	90.636	86.818	85.545	93.091	85.545	90.091	93.091	90.091
Variance	27.800	16.855	27.800	21.364	16.855	21.364	104.673	158.091	104.673	21.291	158.091	21.291
Observations	11.000	11.000	11.000	11.000	11.000	11.000	11.000	11.000	11.000	11.000	11.000	11.000
Hypothesized mean difference	0.000		0.000		0.000		0.000		0.000		0.000	
Df	19.000		20.000		20.000		19.000		14.000		13.000	
t stat	1.173		2.924		2.048		−1.544		−1.343		0.743	
P(T ≤ t) one-tail	0.128		0.004		0.027		0.070		0.100		0.235	
t critical one-tail	1.729		1.725		1.725		1.729		1.761		1.771	
P(T ≤ t) two-tail	0.255		0.008		0.054		0.139		0.201		0.471	
t critical two-tail	2.093		2.086		2.086		2.093		2.145		2.160	

Table A3. Statistical analysis of effect of digestion method on total recoverable metals in wastewater influent: *t*-test assuming unequal variances for the three spike concentrations

Statistic	Hotplate						Microwave					
	Spike concentration (mg/L)											
	0.10	0.50	0.10	1.0	0.50	1.0	0.1	0.50	0.1	1.0	0.5	1.0
Mean	89.23077	87.07692	89.23077	85.69231	87.07692	85.69231	92.38462	90.46154	92.38462	89.23077	90.46154	89.23077
Variance	120.359	21.57692	120.359	74.23077	21.57692	74.23077	97.08974	23.60256	97.08974	92.19231	23.60256	92.19231
Observations	13	13	13	13	13	13	13	13	13	13	13	13
Hypothesized mean difference	0		0		0		0		0		0	
Df	16		23		18		18		24		18	
t stat	0.651839		0.914589		0.510036		0.631144		0.826528		0.412386	
P(T ≤ t) one-tail	0.26188		0.184948		0.308112		0.26794		0.208323		0.342463	
t critical one-tail	1.745884		1.713872		1.734064		1.734064		1.710882		1.734064	
P(T ≤ t) two-tail	0.523759		0.369896		0.616224		0.535879		0.416647		0.684927	
t critical two-tail	2.119905		2.068658		2.100922		2.100922		2.063899		2.100922	

Table A4. Statistical analysis of effect of digestion method on total dissolved metals in wastewater influent: *t*-test assuming unequal variances for the three spike concentrations

Statistic	Hotplate						Microwave					
	Spike concentration (mg/L)											
	0.10	0.50	0.10	1.0	0.50	1.0	0.1	0.50	0.1	1.0	0.5	1.0
Mean	86.38462	86.92308	86.38462	85.61538	86.92308	85.61538	91.61538	90.92308	91.61538	87.92308	90.92308	87.92308
Variance	45.08974	42.57692	45.08974	128.4231	42.57692	128.4231	107.2564	25.41026	107.2564	90.57692	25.41026	90.57692
Observations	13	13	13	13	13	13	13	13	13	13	13	13
Hypothesized mean difference	0		0		0		0		0		0	
Df	24		20		19		17		24		18	
t stat	−0.20735		0.210554		0.360561		0.216715		0.946498		1.004357	
P(T ≤ t) one-tail	0.418742		0.417683		0.361202		0.415505		0.176664		0.164259	
t critical one-tail	1.710882		1.724718		1.729133		1.739607		1.710882		1.734064	
P(T ≤ t) two-tail	0.837484		0.835366		0.722405		0.831009		0.353328		0.328518	
t critical two-tail	2.063899		2.085963		2.093024		2.109816		2.063899		2.100922	

Table A5. Statistical analysis of effect of digestion method on metal recoveries in tap water: *t*-test assuming unequal variances for the (TR: total recovered metals; TD; total dissolved metals)

Statistic	*t*-test: Two-sample assuming unequal variances							
	TR, heat	TD, heat	TR, micro	TD, micro	TR, heat	TR, micro	TD, heat	TD, micro
Tap water, Richmond (RC)								
Mean	43.96667	60.63333	54.23333	35.2	43.96667	54.23333	60.63333	35.2
Variance	542.1733	1 774.823	752.4133	644.77	542.1733	752.4133	1 774.823	644.77
Observations	3	3	3	3	3	3	3	3
Hypothesized mean difference	0		0		0		0	
Df	3		4		4		3	
t stat	−0.59972		0.88196		−0.49422		0.895556	
P(*T* ≤ *t*) one-tail	0.295483		0.213805		0.323529		0.21824	
t critical one-tail	2.353363		2.131847		2.131847		2.353363	
P(*T* ≤ *t*) two-tail	0.590967		0.42761		0.647059		0.436481	
t critical two-tail	3.182446		2.776445		2.776445		3.182446	
Tap water, Scottsville (SV)								
Mean	52.85	35.9	65.825	53.65	52.85	65.825	35.9	53.65
Variance	2 141.05	847.02	3 459.516	2 292.31	2 141.05	3 459.516	847.02	2 292.31
Observations	4	4	4	4	4	4	4	4
Hypothesized mean difference	0		0		0		0	
Df	5		6		6		5	
t stat	0.620161		0.321067		−0.34675		−0.63359	
P(*T* ≤ *t*) one-tail	0.28116		0.379524		0.370307		0.277097	
t critical one-tail	2.015048		1.94318		1.94318		2.015048	
P(*T* ≤ *t*) two-tail	0.56232		0.759048		0.740614		0.554193	
t critical two-tail	2.570582		2.446912		2.446912		2.570582	
Tap water, Mkhondeni (MN)								
Mean	40.025	25.775	77.9	36.775	40.025	77.9	25.775	36.775
Variance	923.9492	596.2292	4601.36	954.3025	923.9492	4601.36	596.2292	954.3025
Observations	4	4	4	4	4	4	4	4
Hypothesized mean difference	0		0		0		0	
Df	6		4		4		6	
t stat	0.730967		1.103489		−1.01907		−0.5587	
P(*T* ≤ *t*) one-tail	0.246173		0.165867		0.182896		0.298291	
t critical one-tail	1.94318		2.131847		2.131847		1.94318	
P(*T* ≤ *t*) two-tail	0.492346		0.331735		0.365791		0.596582	
t critical two-tail	2.446912		2.776445		2.776445		2.446912	
Tap water, Woodlands (WL)								
Mean	52	56.925	38.225	31.25	52	38.225	56.925	31.25
Variance	2 200.987	2 925.583	614.3492	483.07	2200.987	614.3492	2 925.583	483.07
Observations	4	4	4	4	4	4	4	4
Hypothesized Mean Difference	0		0		0		0	
Df	6		6		5		4	
t stat	−0.13757		0.421103		0.519226		0.879527	
P(*T* ≤ *t*) one-tail	0.447541		0.344174		0.31288		0.214391	
t critical one-tail	1.94318		1.94318		2.015048		2.131847	
P(*T* ≤ *t*) two-tail	0.895081		0.688348		0.62576		0.428782	
t critical two-tail	2.446912		2.446912		2.570582		2.776445	
Tap water, Boughton (BT)								
Mean	45.825	26.275	36.9	43.325	45.825	36.9	26.275	43.325
Variance	989.7892	612.5825	753.2867	1 285.729	989.7892	753.2867	612.5825	1 285.729
Observations	4	4	4	4	4	4	4	4
Hypothesized mean difference	0		0		0		0	
Df	6		6		6		5	
t stat	0.976776		−0.28457		0.427543		−0.78266	
P(*T* ≤ *t*) one-tail	0.183201		0.392769		0.341951		0.234628	
t critical one-tail	1.94318		1.94318		1.94318		2.015048	
P(*T* ≤ *t*) two-tail	0.366403		0.785538		0.683903		0.469257	
t critical two-tail	2.446912		2.446912		2.446912		2.570582	

Table A6. Statistical analysis of effect of digestion method on metal recoveries in river water: *t*-test assuming unequal variances for the (TR: total recovered metals; TD; total dissolved metals)

Statistic	*t*-test: Two-sample assuming unequal variances							
	TR, heat	TD, heat	TR, micro	TD, micro	TR, heat	TR, micro	TD, heat	TD, micro
River water, Bishopstowe (BS)								
Mean	28.16667	38.53333	43.433333	35.8	28.16667	43.43333	38.53333	35.8
Variance	139.6933	1 139.103	546.20333	832.36	139.6933	546.2033	1 139.103	832.36
Observations	3	3	3	3	3	3	3	3
Hypothesized mean difference	0		0		0		0	
Df	2		4		3		4	
t stat	−0.50211		0.3560914		−1.00966		0.106625	
$P(T \le t)$ one-tail	0.332709		0.3698797		0.193513		0.46011	
t critical one-tail	2.919986		2.1318468		2.353363		2.131847	
$P(T \le t)$ two-tail	0.665417		0.7397594		0.387027		0.92022	
t critical two-tail	4.302653		2.7764451		3.182446		2.776445	
River water, Camps Drift (CD)								
Mean	35.55	49.85	62.366667	45.1	35.55	62.36667	49.85	45.1
Variance	49.005	741.125	446.33333	954.79	49.005	446.3333	741.125	954.79
Observations	2	2	3	3	2	3	2	3
Hypothesized mean difference	0		0		0		0	
Df	1		4		3		3	
t stat	−0.71945		0.7989709		−2.03718		0.180983	
$P(T \le t)$ one-tail	0.301482		0.23453		0.067205		0.433959	
t critical one-tail	6.313752		2.1318468		2.353363		2.353363	
$P(T \le t)$ two-tail	0.602964		0.4690599		0.134411		0.867917	
t critical two-tail	12.7062		2.7764451		3.182446		3.182446	
River water, College Road (CR)								
Mean	47.65	76.5	42.75	55.675	47.65	42.75	76.5	55.675
Variance	616.005	3 872	2 394.47	2 599.836	616.005	2 394.47	3 872	2 599.836
Observations	2	2	4	4	2	4	2	4
Hypothesized mean difference	0		0		0		0	
Df	1		6		4		2	
t stat	−0.60902		−0.365783		0.162736		0.409519	
$P(T \le t)$ one-tail	0.325876		0.3635387		0.439308		0.360927	
t critical one-tail	6.313752		1.9431803		2.131847		2.919986	
$P(T \le t)$ two-tail	0.651751		0.7270773		0.878617		0.721853	
t critical two-tail	12.7062		2.4469119		2.776445		4.302653	
River water, Woodhouse (WH)								
Mean	43.2	41.76667	38.075	70.175	43.2	38.075	41.76667	70.175
Variance	0.5	988.5633	780.79583	1792.269	0.5	780.7958	988.5633	1792.269
Observations	2	3	4	4	2	4	3	4
Hypothesized mean difference	0		0		0		0	
Df	2		5		3		5	
t stat	0.07893		−1.265638		0.366587		−1.01876	
$P(T \le t)$ one-tail	0.472137		0.1307059		0.369128		0.177527	
t critical one-tail	2.919986		2.0150484		2.353363		2.015048	
$P(T \le t)$ two-tail	0.944275		0.2614118		0.738256		0.355053	

Table A7. Results of ANOVA for effect of digestion method (hotplate and microwave) on hotplate and microwave digestion for total recoverable metals in tap, river and wastewater samples

Source of variation	SS	Df	MS	F	*p*-value	F crit
Tap water						
Between groups	8 438.859	9	937.651	0.588687	0.795808	2.210697
Within groups	47 783.49	30	1 592.783			
Total	56 222.34	39				
River water						
Between groups	3 216.133	9	357.3481	0.50683	0.839433	3.020383
Within groups	7 050.645	10	705.0645			
Total	10 266.78	19				